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How to cite:

Heeley, E.L.; Gough, T.; Bras, W.; Gleeson, A.J.; Coates, P.D. and Ryan, A.J. (2005). Polymer processing: Using synchrotron radiation to follow structure development in commercial and novel polymer materials. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 238(1-4) pp. 21-27.

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Version: Accepted Manuscript

Link(s) to article on publisher's website:

<http://dx.doi.org/doi:10.1016/j.nimb.2005.06.012>

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Polymer Processing: using synchrotron radiation to follow structure development in commercial and novel polymer materials

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Abstract:

Exploring the macro and micro-structure development associated with crystallization in polymer materials such as polyethylene and polypropylene can be achieved using Small-and Wide-Angle X-ray Scattering techniques (SAXS/WAXS). Here, SAXS probes the long range ordering or macrostructure and WAXS gives information on the atomic level of ordering (microstructure). Following structure development and hence the crystallization process in polymers, is particularly important as it leads to the stabilisation of the final product. The crystallinity in a polymer material influences its aesthetic and mechanical properties and so to develop useful materials it is essential to have a deep understanding of the kinetics involved with this process, which can be explored with a variety of scattering techniques.

PACS Codes: 01.30.C; 07.85; 89.02; 89.20

Keywords: Small and Wide angle X-ray scattering (SAXS/WAXS), polymer processing, novel comb polymers

Introduction:

Understanding of the crystallization of polymer materials is essential for the prediction of processing methods and thus the related material properties. Crystallization in polymers is still a mystery and so continues to be a well researched topic[1]. Here, several experiments allowing us to follow polymer crystallization have been performed using synchrotron radiation sources: ESRF (France) and the Daresbury SRS (UK). Both quiescent and shear-induced crystallization of polymers have been studied using time resolved SAXS/WAXS techniques with *in-situ* processing instrumentation. For example, quiescent crystallization of polyolefins has been performed with an *in-situ* differential scanning calorimeter (DSC) instrument on the DUBBLE CRG at the ESRF[2]. In comparison shear-induced crystallization has also been investigated by a number of on-line

processing techniques, e.g. a Linkam CSS450 shear instrument[3], a commercial extruder[1,2] and mini re-circulating flow cell (MRFC)[4]. Such shear instrumentation along with simultaneous SAXS/WAXS data collection, has given insights into the crystallization process under the influence of flow during simulated industrial processing conditions. The use of time resolved synchrotron radiation is shown here to be an invaluable in probing such processes and will enable us to expand our understanding of crystallization kinetics with relevance to industrial processing techniques.

Experimental:

The polymers used in these experiments were either commercial polyethylene (PE), Lupolen (BASF), or Daplen isotactic polypropylene (PCD Polymer GmbH) and polyethylene type samples (linear and comb architectures) which have been synthesised by anionic polymerisation methods[5]. Table 1 gives the molecular characteristics for all samples described. In-depth details of quiescent and shear induced crystallization experimental set-ups are given in Heeley *et. al*[6] and Heeley *et. al*[3] respectively. Quiescent crystallization was performed using a Linkam DSC as an *in-situ* device, where the sample is heated to 180°C and then cooled at 50°C/min to the selected crystallization temperature. Then SAXS/WAXS measurements were used to follow the crystallization kinetics and structure development. In comparison, commercial and synthesised PE samples were also subjected to shear induced crystallization using a Linkam CSS450 shearing instrument Here, a fast shear pulse was given to the sample once it has been cooled to the crystallization temperature and SAXS was used to follow the crystallization process. Typical experimental set-ups for DSC and shear devices on the ESRF DUBBLE beamline are shown in Figure 1. Lupolen PE was also extruded from a BX18 AXON[2,7] extruder system. Here, the real time extrusion process has been followed by using 2D SAXS and WAXS techniques to follow the structure development in the extruded polymer tape. Figure 2 shows the extruder system on the Daresbury SRS beamline 16.1. Finally, flow crystallization kinetics in Lupolen PE has been investigated using a mini-re-circulating flow cell (MRFC)[4,8]. Here, continuous flow processing of polymers is followed using SAXS through a slot die device (the geometries of the instrument can be changed) allowing high shear rates to be achieved mimicking industrial injection moulding techniques. Figure 3 shows the MRFC as an *in-situ* instrument on the Daresbury SRS beamline 16.1. These techniques have been used to successfully gain insight into the crystallization of the selected polymer systems and allowed direct comparison to the industrial processing technique used.

Results and Discussion:

Using these on-line processing techniques it has been possible to investigate the development of crystallization and thus macro-structure of a polymer system; some brief results are given here. Figures 4-7 give some examples of the simultaneous SAXS and WAXS results of the crystallization processes using a variety of these processing devices on beamlines. Briefly, Figure 4 shows the quiescent crystallization of Daplen iPP at 130°C, followed by using simultaneous SAXS/WAXS. Here the development of the Bragg crystalline peaks (WAXS) are seen developing at the same time as the lamellar stacking in the SAXS allowing information about the crystallization kinetics to be obtained. However, in further experiments detailed elsewhere [2,4], we have reported that the crystallization kinetics can change and follow non-conventional mechanisms at lower quench depths. Figure

5 shows the developing SAXS from shear crystallization of Lupolen PE and linear/comb blended samples. This has enabled information to be obtained on how the architecture, molecular weight (M_w) and polydispersity of polymers influences the crystallization kinetics. Here, the commercial Lupolen sample shows well oriented SAXS patterns and increased crystallization times after shear compared to that of isothermal crystallization conditions. However, the comb blend sample shows far less oriented SAXS patterns but, again greatly accelerated crystallization rates after shear. This indicates that the long chain branching in the comb sample may be acting as nucleating sites for crystallization but not always resulting in an oriented structure of fibril morphology. In Figure 6 examples of SAXS and WAXS is given from an extruded tape of Daplen iPP, where the obvious structure development changes down the spinline. Here it can be seen that the SAXS pattern shows some oriented structure at higher temperatures but no corresponding Bragg peaks are seen in the WAXS. At lower temperatures there is distinct structure development shown by the SAXS and WAXS patterns. This again, allows insight into the crystallization kinetics during the extrusion processing of polymer tapes. Finally, in Figure 7, SAXS patterns are shown from the crystallization of Lupolen PE having been subjected to flow through a slot die. This is mimicking an industrial processing technique but, the use of temporal X-ray scattering allows the structure development to be followed inside the instrument. Here, the structure development after shear through a particular die geometry is shown by the SAXS patterns. Changing the die slot geometry can alter the rate and type of crystallization hence the macromolecular structure of the polymer, once processed in such an instrument.

Conclusions

Here we have discussed and shown examples of how crystallization of various polymers can be followed during processing with synchrotron radiation. Importantly, the techniques used mimic industrial processing and allow us to relate macromolecular structure development in the material to both the processing parameters and the molecular structure of the polymer. The use of synchrotron radiation and high flux beamlines has enabled these fast processes to be followed successfully. Further developments in processing methods and X-ray beamlines will continue to allow great insight into the highly debated topic of polymer crystallization and in the future will lead to a greater understanding of the processes through out the early to late stages of the structure development.

Acknowledgements

E.L.H was supported by the EPSRC grant (GR/M60415) which provided the beamtime at the Daresbury SRS. The beamtime at the ESRF was provided under the LTP SC777. The authors would like to thank all beamline staff at the SRS and ESRF. Samples were kindly provided by PCD Polymer GmbH, BASF and C. M. Fernyhough (Sheffield chemistry).

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Figure legends:

Figure 1: (A) Linkam DSC , (B) Linkam shear cell and (C) DUBBLE GRG beamline at the ESRF.

Figure 2: (A) Axon BX18 extruder on beamline 16.1 Daresbury SRS, (B) polymer tape being extruded from die head and (C) polymer tape at the beampipe.

Figure 3: (A) MRFC picture and dimensions, (B) schematic of MRFC and (C) MRFC on beamline 16.1 Daresbury SRS.

Figure 4: 1D simultaneous SAXS/WAXS of the isothermal crystallization of Daplen iPP at 130°C.

Figure 5: SAXS of shear induced crystallization and integrated half times ($t_{1/2}$) for comparison with isothermal crystallization kinetics (A) Lupolen PE shear rate 100 s^{-1} for 5 sec, at 109°C and (B) blend of 10% comb10 and 90% linear PE polymers, shear rate 100 s^{-1} for 5 sec, at several temperatures.

Figure 6: Extrusion of Daplen iPP: SAXS and WAXS examples down the spinline (lower temperature more structure development) and a graph showing the change in long spacing of the meridional SAXS intensity down the spinline.

Figure 7: Development of SAXS during the crystallization of Lupolen PE at 105°C having been sheared in the MRFC instrument.

Table 1: Molecular parameters of samples used to investigate crystallization kinetics using polymer processing techniques.

Sample	$M_w/\text{kg mol}^{-1}$	M_w/M_n
Lupolen PE	250	13.5
Daplen iPP	622	5.5
Linear A	52.8	1.01
Comb10	Backbone 53.8 Arm ($\times 8$) 14.8	1.02

Figure 1.

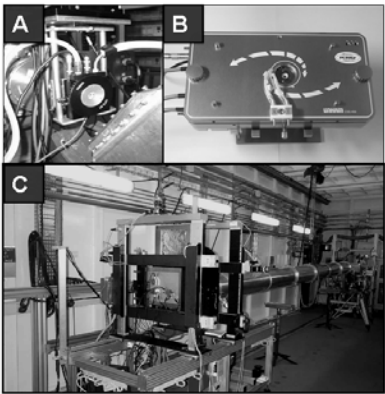


Figure 2.

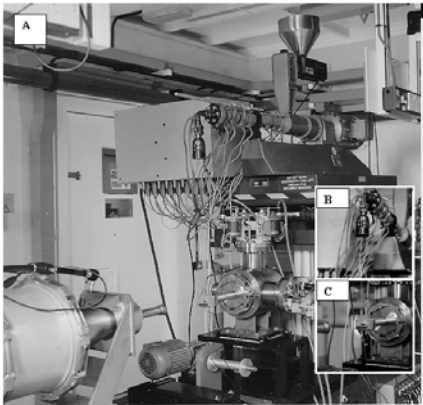


Figure 3.

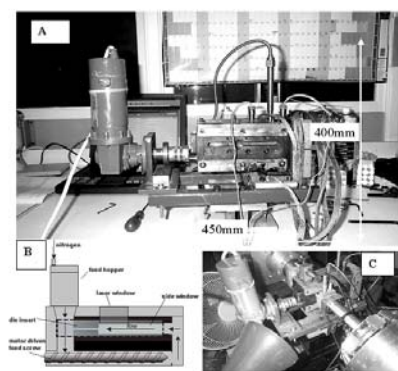


Figure 4.

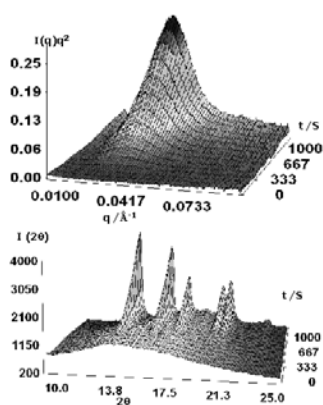


Figure 5.

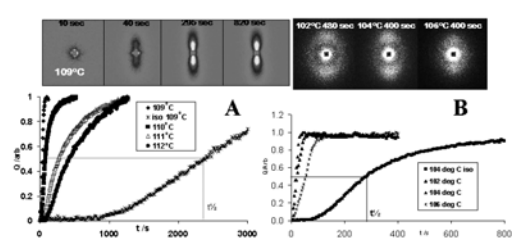


Figure 6.

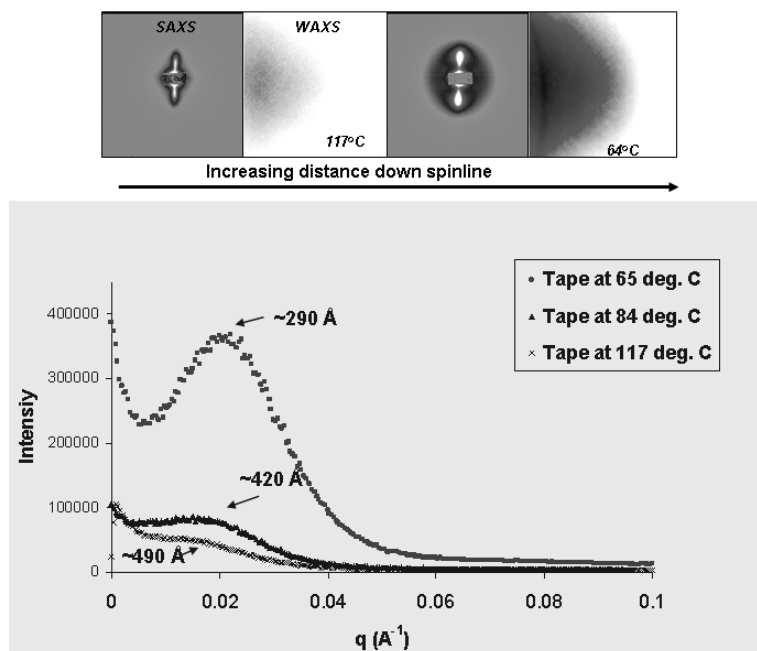


Figure 7.

